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Specification and Drawings, as originally filed, with Application for Patent Serial No: 2,405,635, on September 27, 2002; by CO2 SOLUTIONS INC., assignee of Sylvie Fradette and Jean Ruel, for "A Process and a Plant for the Production of Useful Carbonated Species and for the Recycling of Carbon Dioxide Emissions from Power Plants".

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# A PROCESS AND A PLANT FOR THE PRODUCTION OF USEFUL CARBONATED SPECIES AND FOR THE RECYCLING OF CARBON DIOXIDE EMISSIONS FROM POWER PLANTS

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#### FIELD OF THE INVENTION

The present invention relates generally to the field of processes and apparatuses used for energy production in fossil-fuel power plants. More specifically, it concerns a process and a plant for the sequestration of carbon dioxide emissions emanating from fossil-fuel power plants, and for the production of useful carbonated species.

### **BACKGROUND OF THE INVENTION**

Fossil-fuel power plants produce the main part of the energy actually consumed worldwide. Energy is generated from the combustion of fossil-fuels such as coal, natural gas and fuel oil. The use of biomass to fuel the power plant is also within the scope of this invention. Main exhaust gases formed from such processes may be  $CO_2$ ,  $SO_2$  and  $NO_x$  depending on the nature of the fuel used. Treatment systems are already available for reducing  $SO_2$  and  $NO_x$  emissions. However,  $CO_2$  emissions from fossil-fuel power plant are not contained or reduced. These  $CO_2$  emissions thus contribute to increase the atmospheric concentration of  $CO_2$ , the most important greenhouse gas. It is known that such an increase in greenhouse gases causes climate changes which could lead to various environmental problems, such as an increase in violent weather events, significant temperature warming in specific areas, changes in the precipitation pattern trends and a rise of ocean level.

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Moreover, in the next century, a significant increase of carbon dioxide concentrations is expected unless energy production systems reduce their emissions to the atmosphere. Carbon sequestration consisting of carbon capture, separation and storage or reuse represent potent ways to stabilize and eventually reduce concentration of atmospheric CO<sub>2</sub>.

Several technologies, based on carbon sequestration, are being studied by academic and industrial groups. They are transformation by algae, sequestration of in oceans, storage in depleted oil and natural gas wells and dissolution of pressurized  $CO_2$  in water tables.  $CO_2$  can also be transformed into more geologically stable forms, such as calcium carbonate.

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Transformation of  $CO_2$  with algae involves the use of algal photosynthesis. The gas emitted by power stations would thus be directly introduced in basins located nearby. The selected algae must therefore support these environments with harsh conditions. The algae produced could be dried up and used as fuel to supply the power station. This approach reduces the required fuel to supply power, but does not eliminate completely  $CO_2$  production.

Sequestration in oceans consists in pumping the carbon dioxide to be disposed of to depths of 1,000 metres below sea level. The technique is based on the fact that CO<sub>2</sub> possesses a higher density than water. It is believed that CO<sub>2</sub> will sink to the bottom of oceans where lakes of liquid carbon dioxide will be formed. However, as yet, the environmental impact of this technology has not been demonstrated.

Oil and natural gas wells are capable of supporting enormous pressures without leakage. They are therefore an ideal location for the storage of compressed CO<sub>2</sub>. In the petroleum industry, the injection of CO<sub>2</sub> in wells to enhance oil recovery is a widely used technique. However, this method only constitutes a temporary storage, since in the medium term the displacements of the earth's crust are capable of bringing about a release of CO<sub>2</sub>. Moreover, although there are hundreds of depleted sited around the world, their total capacity is after all limited and there is an obligation to land case the geological formations involved.

The deep water tables are distributed throughout the globe. They generally include salt water and are separated from the surface water tables which constitute the drinking water supplies. The water contained in these natural reservoirs can dissolve the pressurized CO<sub>2</sub> and even disperse it in the geological formations. However, the

implementation of this technology must always imply a strong concern regarding the proximity of the water tables with the  $CO_2$  emission sources.

Although some solutions have been proposed in the past for reducing CO<sub>2</sub> emissions in general, few of them have shown to be efficient or commercially viable for different reasons. Moreover, a very few, if not none, of the solutions proposed specifically apply to CO<sub>2</sub> emissions from fossil-fuel power plant. Thus, there is still a need for a solution for reducing those CO<sub>2</sub> emissions from fossil-fuel power plant. With the general concern throughout the world with respect to the urgency of finding a solution to the problem of emissions of greenhouse gases, this need is even more obvious.

#### SUMMARY OF THE INVENTION

An object of the present invention is to provide a process and a fossil-fuel power plant that satisfy the above mentioned need

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This process is characterised in that it comprises a step where the CO<sub>2</sub> emissions are transformed by means of a biological process into different carbonated species, such as calcium carbonate, a geological natural product. CO<sub>2</sub> transformation takes place inside a bioreactor and is performed by an enzyme which accelerates its transformation into bicarbonate in an aqueous environment. The bicarbonate can then be precipitated into a stable solid product.

This invention thus proposes the integration of a  $CO_2$  transformation process into a fossil-fuel power plant in order to produce bicarbonate species which are useful by-products, and thereby reducing at the same time the  $CO_2$  emissions. This  $CO_2$  transformation process is based on a biological reactor which enables  $CO_2$  transformation into bicarbonate in an aqueous environment. The  $CO_2$  is then precipitated into a stable solid product, safe for the environment.

### CO<sub>2</sub> production in a fossil fuel power plant

CO<sub>2</sub> is produced during combustion of fossil fuels such as coal, natural gas or fuel oil (Equation 1). In the case of a coal power plant, the heat released during this combustion is used to heat water and produce steam which then passes through steam turbines coupled to electric alternators leading to electricity generation. In the case of a natural gas power plant, the fuel is burned directly in gas turbines coupled to electric alternators.

10  $C_xH_y + (x+y/4)O_2 \xrightarrow{\Delta} x CO_2 + y/2H_2O$ 

Equation 1

Other gases may also be produced by combustion, namely SO<sub>2</sub> and NO<sub>x</sub> given the original sulfur and nitrogen content of the used fuel. These other gases are encountered mainly in coal power plants.

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Flue gas exhausting from combustion chambers and containing  $CO_2$  is discharged directly to the atmosphere. In the context of this invention,  $CO_2$  emissions are treated and reduced by the proposed biological process.

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In the case of coal power plants, flue gas has first to be cooled in order to have a temperature that does not lead to biocatalysts denaturation (free and/or immobilized). Gas cooling is obtained with any type of heat exchanging device, and the recovered energy is used to increase the process efficiency. The heat could, for example, be used to pre-heat the air required for combustion, or to supply energy for additional turbines. The gas is then treated to remove excess ash, SO<sub>2</sub> and NO<sub>x</sub> in order that the gas be of adequate quality for the biological process. Ash can be removed using units such as electrostatic precipitator and fabric filters. SO<sub>2</sub> can be removed using units scrubbers and NO<sub>x</sub> using burners or catalytic systems leading to the conversion of NO<sub>x</sub> to N<sub>2</sub> and H<sub>2</sub>O.

## CO<sub>2</sub> transformation in a biological process

Gas phase containing CO<sub>2</sub> with appropriate level of ash, SO<sub>2</sub>, NO<sub>x</sub> and at appropriate temperature an pressure, are then fed to the biological process enabling CO<sub>2</sub> transformation into bicarbonate and hydrogen ions. This biological process comprises a biological reactor where CO<sub>2</sub> transformation takes place. This transformation is catalyzed by a biocatalyst accelerating CO<sub>2</sub> transformation. The biocatalyst is a biological entity which can transform a substrate in one or more products. The biocatalyst may be an enzyme, a cellular organelle (mitochondrion, membrane, etc.), animal, vegetal or human cells. The biocatalyst is preferably the enzyme carbonic anhydrase but may be any biological catalyst enabling CO<sub>2</sub> transformation. CO<sub>2</sub> transformation reaction is the following:

CO2 +H2O ₹¥ HCO1+H+

Equation 2

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This reaction is natural. It is at the basis of CO<sub>2</sub> transportation and removal phenomenon in the human body and in most living beings.

The biological catalyst may be free or immobilized inside the biological reactor. An example of a bioreactor which could be used for biological transformation of CO<sub>2</sub> is described in Process and Apparatus for the Treatment of Carbon Dioxide with carbonic anhydrase (Blais et al. )(CA 2,291,785). In this process, carbonic anhydrase is immobilized onto a solid support. Solid supports can be made of various organic and inorganic material and have shapes proper to packed columns. The gas phase containing CO<sub>2</sub> enters at the bottom of the packed column and the liquid phase enters at the top of the column. Both phases flow counter currently and close contact of liquid and gas phases is promoted by a solid support having immobilized enzymes on its surface: Gaseous CO<sub>2</sub> is then transferred to the liquid phase where it dissolves and then is transformed according to Equation 2. The liquid flows in and out of the column and is treated for precipitating the bicarbonate lons produced by the bioreaction.

Another biological reactor with free and/or immobilized enzymes for CO<sub>2</sub> transformation into bicarbonate is the following:

The bioreactor consists of a chamber containing biocatalyst particles. The gas to be treated enters at the bottom of the chamber. A diffusion system is responsible for the uniform distribution of the gas phase at the bottom of the chamber and is designed for minimum bubbles diameter. These conditions are required to optimize gas-liquid contact. An agitation devices (magnetic or mechanical) can also be used to assure uniform biocatalyst distribution. Liquid phase enables gas dissolution and thus the 10 biocatalytic reaction. In this process, the biocatalyst (preferably carbonic anhydrase, but may be any biological catalyst) is either free in the liquid phase and/or immobilized onto a solid support and/or entrapped inside a solid matrix. These particles are moving freely in the liquid and are prevented from exiting the chamber by a membrane or filter. The liquid flows in and out of the chamber and is treated for 15 precipitation of the bicarbonate ions produced by the bioreaction.

As mentioned, bicarbonate ions produced in these two types of bioreactors have to be precipitated and finally sequestrated. This precipitation is obtained by combining bicarbonate ions to cations. Cations used may be calcium, barium, magnesium, sodium or any cation that could lead to the formation of carbonates or bicarbonates salts. As shown in Figure 2, a potential source of cations is the reagent solution coming out of the SO<sub>2</sub> treatment unit. Bicarbonate ions can also be used directly in other chemical or biological processes.

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In summary, CO2 is to be transformed, for example into calcium carbonate, in the biological process, according to the following reactions

CO<sub>2</sub> dissolved + H<sub>2</sub>O 
$$\Rightarrow$$
 H<sup>+</sup> + HCO<sub>3</sub><sup>-</sup>

HCO<sub>3</sub><sup>-</sup>  $\Rightarrow$  H<sup>+</sup> + CO<sub>3</sub><sup>2-</sup>

CO<sub>3</sub><sup>2-</sup> + Ca<sup>2+</sup>  $\Rightarrow$  CaCO<sub>3</sub>

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The coupling of the biological process for CO<sub>2</sub> removal and transformation to a fossilfuel power plant leads to a reduction of CO<sub>2</sub> emissions into the atmosphere and an increase energy efficiency of the plant. Furthermore, the required cooling of the flue gas enabling proper operation of the bioreactor is coupled to energy recovery systems that produce additional power output for the power plant.

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#### **DESCRIPTION OF PREFERRED EMBODIMENTS**

10 Two schematic drawings are provided to describe the invention in the context of power plant processes.

Figure 1: Integration of biological process to energy generation processes

15 In this diagram, the nature of the fossil fuel (coal or natural gas) used to power the plant leads to two different branches.

In the case of coal, the fuel is burned in a combustion chamber, the heat is used to produce steam from water, and the steam propels turbines and alternators producing electric power. The flue gas exiting the combustion chamber is treated to remove ash, NOx and/or  $SO_2$ . In the current configuration of power plants, the gas is finally exhausted by a stack.

In the context of this invention, the gas is not exhausted at this stage, but rather sent to additional heat exchangers and energy recovery systems to cool it down to an adequate temperature for the biological process. Energy is produced by this step. The gas is then treated to remove additional contaminants that may be harmful to the biological process, and finally, CO<sub>2</sub> is remove by the bioreactor and the gas is blown to the atmosphere.

In the case of natural gas, the fuel is burned directly in the turbine, and the intermediary step of steam production in not present in the main power production

stage, although it may be used in subsequent heat recovery stages. The rest of the process is analog to that of the left branch (coal).

Figure 2: Integration of the biological process to the SO<sub>2</sub> treatment unit

This diagram explains the cross-linking that may be performed between the biological process and the SO<sub>2</sub> treatment unit present in the current power plant process. To remove SO<sub>2</sub> from the flue gas, a reagent solution is required. An analog solution is also required for the biological process. This solution, readily available from either sub-process may be used in closed loop for both processes.

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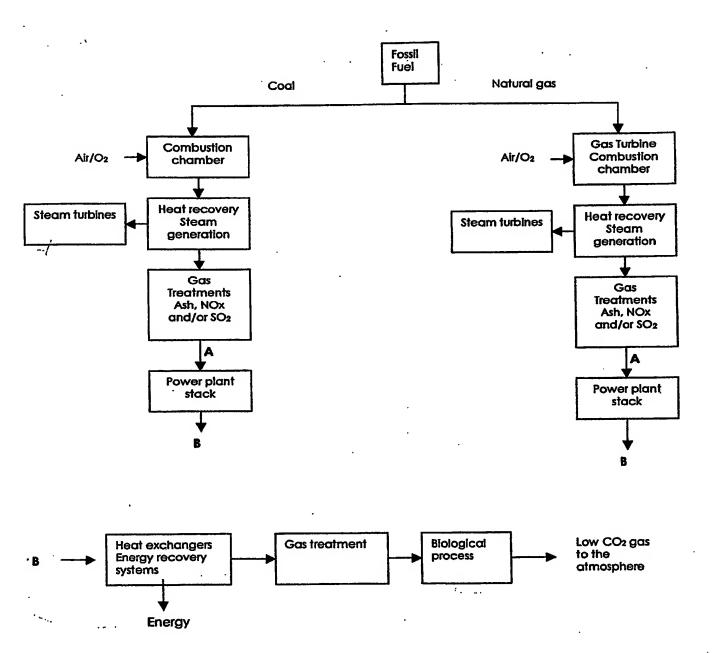


Figure 1

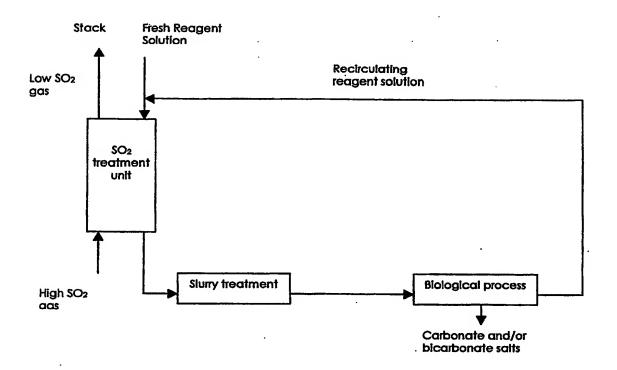


Figure 2

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